

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 April 2003 (10.04.2003)

PCT

(10) International Publication Number
WO 03/029331 A1

- (51) International Patent Classification⁷: C08J 3/05, (74) Agent: LOCKLAR, Michael; Baker Botts, L.L.P., One Shell Plaza, 910 Louisiana, Houston, TX 77002-4995 (US).
- (21) International Application Number: PCT/US02/30816 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 27 September 2002 (27.09.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/325,667 28 September 2001 (28.09.2001) US (84) Designated States (*regional*): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR).
- (71) Applicant: CONOCO, INC. [US/US]; 600 North Dairy Ashford, Houston, TX 77079-1175 (US). Published: — with international search report
- (72) Inventors: JOHNSTON, Ray, L.; 800 Michael Lane, Ponca City, OK 74604 (US). SMITH, Kenneth, W.; 302 N. Main Street, Tonkawa, OK 74653 (US). For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF MANUFACTURING DRAG-REDUCING POLYMER SUSPENSIONS

(57) Abstract: A drag-reducing suspension is described, along with a process for manufacturing the drag-reducing suspension. The drag-reducing suspension is easily transportable, non-hazardous, easily handled, and provides a significant increase in drag-reducing capability over existing products.

WO 03/029331 A1

METHOD FOR MANUFACTURING DRAG-REDUCING POLYMER SUSPENSIONS

The present invention relates to drag-reducing polymer suspensions and their
5 method of manufacture. More specifically, this invention relates to a method for
preparing an ultra-high molecular weight hydrocarbon soluble polymer suspension.

A drag-reducing agent is one that substantially reduces the friction loss that
results from the turbulent flow of a fluid. Where fluids are transported over long
distances, such as in oil and other hydrocarbon liquid pipelines, these friction losses
10 result in inefficiencies that increase equipment and operations costs. Ultra-high
molecular weight polymers are known to function well as drag-reducing agents,
particularly in hydrocarbon liquids. In general, drag reduction depends in part upon the
molecular weight of the polymer additive and its ability to dissolve in the hydrocarbon
under turbulent flow. Effective drag-reducing polymers typically have molecular
15 weights in excess of five million.

Drag-reducing polymers are known in the art. Representative, but non-
exhaustive, samples of such art are: U.S. Pat. No. 3,692,676, which teaches a method
for reducing friction loss or drag for pumpable fluids through pipelines by adding a
minor amount of a high molecular weight, non-crystalline polymer; and U.S. Pat. No.
20 3,884,252, which teaches the use of polymer crumb as a drag-reducing material. These
materials are extremely viscoelastic and, in general, have no known use other than as
drag-reducing materials. However, the very properties that make these materials
effective as drag-reducing additives make them difficult to handle because they have a
severe tendency to cold flow and reaggregate even at subambient temperatures.

Under conditions of pressure, such as stacking or palleting, cold flow is even more intense and reagglomeration occurs very quickly.

The general propensity of non-crosslinked elastomeric polymers (elastomers) to cold flow and agglomerate is well-known. Polymers of this sort cannot be pelletized or put into discrete form and then stored for any reasonable period of time without the materials flowing together to form large agglomerates. Because of such difficulties, elastomers are normally shipped and used as bales. However, such bales must be handled on expensive equipment and cannot be pre-blended. In addition, polymers such as the drag-reducing additives described are not susceptible to such balings, since cold flow is extremely severe. Further, dissolution time for such drag-reducing materials from a polymer state in the flowing hydrocarbons to a dissolved state is so lengthy as to severely reduce the effectiveness of this material as a drag-reducing substance.

Numerous attempts have been made to overcome the disadvantages inherent in cold-flowing polymers. Representative, but non-exhaustive, of such art is that described in U.S. Pat. No. 3,791,913, wherein elastomeric pellets are surface cured, *i.e.*, vulcanized to a minor depth in order to maintain the unvulcanized interior of the polymer in a "sack" of cured material, and U.S. Pat. No. 4,147,677, describing a method of preparing a free-flowing, finely divided powder of neutralized sulfonated elastomer by admixing with fillers and oils. This reference does not teach a method for making free-flowing powders of non-elastomeric material. U.S. Pat. No. 3,736,288 teaches solutions of drag-reducing polymers in inert, normally liquid vehicles for addition to liquids flowing in conduits. A "staggered dissolution" effect is provided by

varying the size of the polymer particles. Suspension or surface-active agents can also be used. While directed to ethylene oxide polymers, the method is useful for hydrocarbon-soluble polymers as well. U.S. Pat. No. 4,088,622 describes a method of making an improved, molded drag-reducing coating by incorporating antioxidants,
5 lubricants, and plasticizers and wetting agents in the form of a coating which is bonded directly onto the surface of materials passing through a liquid medium. U.S. Pat. No. 4,340,076 teaches a process for dissolving ultra-high molecular weight hydrocarbon polymer and liquid hydrocarbons by chilling to cryogenic temperatures comminuting the polymer formed into discrete particles and contacting these materials at near
10 cryogenic temperatures with the liquid hydrocarbons to more rapidly dissolve the polymer. U.S. Pat. No. 4,341,078 immobilizes toxic liquids within a container by injecting a slurry of cryogenically ground polymer particles while still at cryogenic temperatures into the toxic liquid. U.S. Pat. No. 4,420,440 teaches a method for collecting spilled hydrocarbons by dissolving sufficient polymer to form a non-flowing
15 material of semisolid consistency by contacting said hydrocarbons with a slurry of cryogenically comminuted ground polymer particles while still at cryogenic temperatures.

Some current drag-reduction systems inject a drag-reducing polymer solution containing a high percentage of dissolved, ultra-high molecular weight polymer into
20 conduits containing the hydrocarbon. The drag-reducing polymer solution is normally extremely thick and difficult to handle at low temperatures. Depending upon the temperature of the hydrocarbon and the concentration at which the drag-reducing polymer solution is injected, significant time elapses before dissolution and resulting

drag reduction. Solid polymers of these types can take days to dissolve in some cases, even though drag reduction is greatly enhanced once dissolution has finally occurred. Also, such ultra-high molecular weight polymer solutions become very viscous as polymer content increases, in some cases limiting the practical application of these solutions to those containing no more than about 15 weight percent polymer. This makes complex equipment necessary for storing, dissolving, pumping, and injecting metered quantities of drag-reducing material into flowing hydrocarbons.

Another way to introduce ultra-high molecular weight polymers into the flowing hydrocarbon stream is through a suspension. The ultra-high molecular weight polymers are suspended in a liquid that will not dissolve or will only partially dissolve the ultra-high molecular weight polymer. This suspension is then introduced into the flowing hydrocarbon stream. The tendency of the ultra-high molecular weight polymers to reaggregate makes manufacture of these suspensions difficult. A way of controlling the tendency of the ultra-high weight polymers to reaggregate is to partially surround the polymer particles with a partitioning agent, occasionally termed a coating material, to reduce the ability of these polymers to reaggregate. U.S. Pat. No. 4,584,244, which is hereby incorporated by reference, describes a process whereby the polymer is ground and then coated with alumina to form a free-flowing powder. Other examples of partitioning agents used in the art include talc, tri-calcium phosphate, magnesium stearate, silica, polyanhydride polymers, sterically hindered alkyl phenol antioxidants, and graphite. Some processes using a "coating agent" (a term which includes some of the compounds defined above as "partitioning agents"), such as those described in U.S. Patent Nos. 4,720,397, 4,826,728, and 4,837,249,

demand that the polymer be surrounded by multiple layers of a coating agent to protect the core from exposure to water and oxygen. These processes, to be effective, require a vast amount of coating agent. Further, the processes are rarely useful, as coating agent typically will not stick to itself. Further, the compositions created by these processes
5 would be expected to have dissolution problems, as the hydrocarbon would be unable to reach the polymer core due to the multiple layers of coating agent. Additionally, the processes described in these patents require that the polymer be coated with the coating agent while within an inert atmosphere, *i.e.*, one that is free from oxygen and water. This requires special, vapor-tight equipment that is expensive to maintain.

10 What is needed is a process for manufacturing a drag-reducing agent that does not require an inert environment and huge amounts of partitioning agent. The composition should be easily dissoluble in the hydrocarbon. Finally, the composition should be suspended in a fluid for easy transport and injection into the hydrocarbon.

Accordingly, methods of producing a drag-reducing suspension are disclosed
15 herein. One embodiment of the present invention is drawn to a method for the preparation of a drag-reducing polymer suspension wherein an ultra-high molecular weight polymer is mixed with an atmosphere containing a refrigerant and oxygen, air or mixture of oxygen and air. The polymer is then ground below the glass transition temperature of the polymer to form ground polymer. The ground polymer is then
20 mixed with a suspending fluid to form the drag-reducing polymer suspension. In another embodiment of the present invention, drag-reducing polymer suspension is prepared by cooling an ultra-high molecular weight polymer to less than about 30°C. The polymer is then chopped to form chopped polymer and then pre-cooled to a

temperature below the glass transition temperature of the polymer in a pre-cooler apparatus. The chopped polymer is mixed with a partitioning agent and oxygen, air, or mixtures thereof are injected. The polymer/partitioning agent mixture is then ground at a temperature below the glass transition temperature of the polymer and mixed with a
5 suspending fluid above the glass transition temperature.

One advantage of the present invention is that the drag-reducing polymer suspension is easily transportable and does not require pressurized or special equipment for storage, transport, or injection. Another advantage is that the drag-reducing polymer is quickly dissolved in the flowing hydrocarbon stream. Still another
10 advantage of the present invention is that reagglomeration of the drag-reducing polymers is greatly reduced, allowing for easier handling during manufacture. Another advantage of the present invention is that the drag-reducing polymer suspension is stable, allowing a longer shelf life and balancing of customer demand with manufacturing time. Additionally, an inert environment is not required for manufacture
15 of the drag-reducing polymer.

Figure 1 is a schematic of the apparatus for manufacturing the drag-reducing polymer suspension.

In the present invention, ultra-high molecular weight polymers are ground at temperatures below the glass transition temperature of the polymer or polymer blends,
20 and then mixed in a suspending fluid. These polymers are generally not highly crystalline. An ultra-high molecular weight polymer typically has a molecular weight of greater than 1 million, preferably more than 5 million. Glass transition temperatures vary with the type of polymer, and typically range between -10°C and -100°C (14°F and -148°F). This temperature can vary depending upon the glass transition point of

the particular polymer or polymer blend, but normally such grinding temperatures must be below the lowest glass transition point of any polymer that comprises a polymer blend.

A preferred ultra-high molecular weight polymer is typically a linear poly(α -olefin) composed of monomers with a carbon chain length of between four and twenty carbons or mixtures of two or more such linear poly(α -olefins). Typical examples of these linear poly(α -olefins) include, but are not limited to, poly(α -octene), poly(α -decene) and poly(α -dodecene). The ultra-high molecular weight polymer may also be a copolymer, *i.e.*, a polymer composed of two or more different types of monomers, as long as all monomers used have a carbon chain length of between four and twenty carbons. Other polymers of a generally similar nature that are soluble in the liquid hydrocarbon will also function in the invention.

As shown in Figure 1, the ultra-high molecular weight polymer is conveyed to coarse chopper 110. Coarse chopper 110 chops large chunks of polymer into small polymer pieces, typically between 0.5 to 1.75 centimeters (1/4 inch to 5/8 inch) in diameter. While coarse chopper 110 may be operated at ambient temperatures, it is preferable to cool the polymer in coarse chopper 110 to less than 30°C (85°F). The polymer in coarse chopper 110 may be cooled either internally or externally or both, with a liquid gaseous or solid refrigerant or a combination thereof, but most commonly by spraying a liquid refrigerant into coarse chopper 110, such as liquid nitrogen, liquid helium, liquid argon, or mixtures of two or more such refrigerants. It may be advantageous to pre-cool coarse chopper 110 prior to introduction of the polymer. The pre-cooling of the coarse chopper step may be accomplished by methods similar to

those used for cooling the polymer in coarse chopper 110. A small amount of a partitioning agent, typically less than about 10% and preferably less than about 8% by weight of the total mixture, may be used in coarse chopper 110 in order to prevent agglomeration of the small polymer pieces. Partitioning agents include calcium
5 stearate, alumina, talc, clay, tri-calcium phosphate, magnesium stearate, polyanhydride polymers, sterically hindered alkyl phenol oxidants, graphite, and stearamide. Partitioning agents should be compatible with the hydrocarbon fluid and should be non-reactive or minimally reactive with the polymer, suspending fluid, and grinding aid. Individual particles of the partitioning agent added to coarse chopper 110 must be small
10 enough to reduce re-agglomeration of the small polymer pieces to an acceptable level. Typically, the particles of the partitioning agent added to coarse chopper 110 are coarse to fine-sized, able to pass through a 140 mesh screen.

Coarse chopper 110 need not be vapor-tight, and the atmosphere within coarse chopper 110, while typically enriched in the refrigerant from the cooling process,
15 normally contains substantial oxygen and water vapor from the ambient air.

The small pieces of polymer and partitioning agent formed in coarse chopper 110 are then transported to pre-cooler 120. This transport may be accomplished by any number of typical solids handling methods, but is most often accomplished through the use of an auger or a pneumatic transport system. Pre-cooler 120 may be an enclosed
20 screw conveyor with nozzles for spraying a liquid refrigerant, such as liquid nitrogen, helium, argon, or mixtures thereof, onto the small polymer pieces. Like coarse chopper 110, pre-cooler 120 is often not vapor-tight and contains oxygen and water vapor

present in the ambient air. While a gaseous refrigerant may also be used alone, the cooling efficiency is often too low.

In addition to the refrigerant, air should be injected into the pre-cooler. During grinding, free radicals are formed on the surface of the polymer particles. These surface free radicals will react with oxygen present in the cryomill. By reducing the surface free radicals, surface tackiness is also reduced, making the polymer less likely to reagglomerate in downstream equipment. Ambient air may be used, which is most often cooled by partial expansion. Liquid or gaseous oxygen may also be injected in place of air. Enough air or oxygen should be added to react all of the surface free radicals, generally at least 1%. An oxygen level in the atmosphere of the pre-cooler of at least 4% is preferred, with a most preferred level of 6% (all in volume percent). Oxygen levels should not be allowed to reach flammable/explosive limits, as the later cryogrinding step produces a polymer dust. It is therefore important to either limit the oxygen level in the atmosphere around the polymer to an amount below the flammability limits of the particular polymer/partitioning agent combination, or to introduce other flammability inhibitors.

In one alternate embodiment of the present invention, a grinding aid may be added to the ultra-high molecular weight polymer prior to cooling in pre-cooler 120. A preferred grinding aid is a material with a melting point of between -100°C to 25°C (-148°F to 77°F), or a material that is totally soluble in the suspending fluid under the conditions disclosed herein when the suspension is produced in mixing tank 150. Examples of grinding aids include ice (frozen water), sucrose, glucose, lactose, fructose, dextrose, sodium saccharin, aspartame, starches, solid propylene carbonate,

solid ethylene carbonate, solid t-butyl alcohol, solid t-amyl alcohol, cyclohexanol, phenol, and mixtures thereof. If such solids are in liquid form at ambient temperatures, they must not be a solvent for the ultra-high molecular weight polymer and should not be a contaminant or be incompatible with the hydrocarbon liquid or mixture for which
5 drag reduction is desired. The grinding aid particles may be of any shape, but are typically crushed, or in the form of pellets or cubes. The grinding aid particles are preferably of equal size or smaller than the small polymer pieces and are more preferably between 1 mm and 6 mm (1/32 inch to 1/4 inch) in diameter. While the amount of grinding aid added is not critical, it is typically added so that the
10 polymer/grinding aid mixture is between about 1% to about 50% by weight of the grinding aid by weight of the total mixture, with the balance being high molecular weight polymer. The use of the grinding aid allows reduction in the amount of partitioning agent required.

In addition to the grinding aid, partitioning agent is typically added to pre-
15 cooler 120. The amount of partitioning will vary depending on a number of factors, including the efficacy of a particular partitioning agent, the hydrocarbon in which the polymer will eventually be dissolved, and the polymer type itself. Generally, the amount of partitioning agent will be less than 50% of the total weight of the polymer/grinding aid/partitioning agent mixture, more frequently less than 35%. As
20 those of skill in the art will appreciate, reducing the amount of partitioning agent will typically decrease the ratio of partitioning agent: polymer and reduce shipping weight. However, as the partitioning agent acts to reduce agglomeration of polymer particles, reducing the concentration of partitioning agent below an appropriate level will make

handling difficult. Nevertheless, formation of any multiple-layer shell of partitioning agent around the polymer particles is undesirable and should be avoided where possible. Polymer added to pre-cooler 120 may be of larger-sized particles than that added to coarse chopper 110, for instance, small spheres or chunks, as long as the
5 particles can be ground in the cryomill. Particle sizes of 25mm and larger may often be accommodated.

The final mixture of polymer/partitioning agent/grinding aid in the pre-cooler is typically: greater than 45% polymer, less than 50% partitioning agent, with the balance being any grinding aid that may have been added. Actual compositions will vary
10 depending on particular conditions.

Pre-cooler 120 reduces the temperature of the small polymer pieces, partitioning agent, and grinding aid ("polymer mixture") to a temperature below the glass transition temperature of the polymer. This temperature is preferably below -130°C (-202°F), and most preferably below -150°C (-238°F). These temperatures may be produced by
15 any known methods, but use of a liquid refrigerant such as that consisting essentially of liquid nitrogen, liquid helium, liquid argon, or a mixture of two or more such refrigerants sprayed directly onto the polymer is preferred, as the resulting atmosphere reduces or eliminates hazards that exist when polymer particles are mixed with an oxygen-containing atmosphere. The rate of addition of the liquid refrigerant may be
20 adjusted to maintain the polymer within the preferred temperature range.

After the polymer mixture is cooled in pre-cooler 120, it is transported to cryomill 130. Again, this transport may be accomplished by any typical solids handling method, but often by an auger or a pneumatic transport system. A liquid

refrigerant may be added to cryomill 130 in order to maintain the temperature of the ultra-high molecular weight polymer in cryomill 130 below the glass transition temperature of the ultra-high molecular weight polymer. The atmosphere within cryomill 130 contains water vapor and oxygen from the ambient air. It is desirable to control the oxygen within cryomill below 15% in order to reduce the risk of conflagration caused by grinding the polymer to dust-sized particles. In one embodiment of the invention, this liquid refrigerant is added to the polymer mixture at the entrance to cryomill 130. The temperature of the cryomill must be kept at a temperature below the glass transition temperature of the polymer. It is preferable to maintain the temperature of the cryomill between -130°C to -155°C (-202°F to -247°F). Cryomill 130 may be any of the types of cryomills known in the art, such as a hammermill or an attrition cryomill. In an attrition cryomill, the polymer mixture is ground between a rapidly rotating disk and a stationary disk to form small particles between 10 and 800 microns in diameter.

The small particles formed in cryomill 130 are then transferred to separator 140. Most of the liquid refrigerant vaporizes in separator 140. Separator 140 acts to separate the primarily vaporized refrigerant atmosphere from the solid particles, and the larger particles from the smaller particles. Separator 140 may be any known type of separator suitable for separating particles of this size, including a rotating sieve, vibrating sieve, centrifugal sifter, and cyclone separator. Separator 140 vents a portion of the primarily vaporized refrigerant atmosphere from cryomill 130 and separates particles into a first fraction with less than about 400 microns in diameter from a second fraction of those with diameters of about 400 microns and above. The second fraction of those particles

of about 400 microns and greater is discarded or preferably returned for recycle purposes to the pre-cooler for regrinding. The first fraction of those particles of less than about 400 microns is then transported to mix tank 150. The 400 micron size for the particles is nominal and may vary or have a distribution anywhere from about 100
5 to about 500 microns, depending on the separator, operating conditions, and desired end use.

While in particle form, care should be taken to keep the temperature of the small particles below the melt temperature of the grinding aid, and preferably below the glass transition temperature of the polymer. High temperatures will typically result in a
10 reagglomeration of the polymer into a solid rubbery mass.

The small particles (the first fraction) are mixed with a suspending fluid in mix tank 150 to form a suspending fluid/polymer particles/grinding aid/partitioning agent mixture. The suspending fluid is any liquid that is a non-solvent for the ultra-high molecular weight polymer and compatible with the hydrocarbon fluid. Water is
15 commonly used, as are other oxygenated solvents including some long chain alcohols such as isooctyl alcohol, hexanol, decanol, and isodecanol, low molecular weight polymers of ethylene or propylene oxide, such as polypropylene glycol and polyethylene glycol, diols such as propylene glycol and ethylene glycol, and other oxygenated organic solvents such as ethylene glycol dimethyl ether and ethylene glycol
20 monomethyl ether, as well as mixtures of these solvents and mixtures of these solvents and water. Mix tank 150 may be any type of vessel designed to agitate the mixture to achieve uniform composition of the suspending fluid polymer particles mixture, typically a stirred tank reactor. Mix tank 150 acts to form a suspension of the polymer

particles in the suspending fluid. The grinding aid particles may melt in the mix tank to mix with the carrier fluid or may dissolve. The temperature of mix tank 150 is generally above the glass transition temperature of the polymer during mixing, although those of skill in the art will appreciate that the polymer particles may be below their glass transition temperature upon initial entry to mix tank 150. Other components may be added to the mix tank before, during, or after mixing the ground polymer particles with the suspending fluid in order to aid the formation of the suspension, and/or to maintain the suspension. For instance, glycols, such as ethylene glycol or propylene glycol, may be added for freeze protection or as a density balancing agent.

10 The amount of glycol added may range from 10% to 60% of the suspending fluid, as needed. A suspension stabilizer may be used to aid in maintaining the suspension of the ultra-high molecular weight particles. Typical suspension stabilizers include talc, tri-calcium phosphate, magnesium stearate, silica, polyanhydride polymers, sterically hindered alkyl phenol antioxidants, graphite and amide waxes such as stearamide, ethylene-bis-stearamide, and oleamide. A wetting agent, such as a surfactant, may be added to aid in the dispersal of the polymer particles to form a uniform mixture. Non-ionic surfactants, such as linear secondary alcohol ethoxylates, linear alcohol ethoxylates, alkylphenol ethoxylates, and anionic surfactants, such as alkyl benzene sulfonates and alcohol ethoxylate sulfates, *e.g.*, sodium lauryl sulfate, are preferred.

20 The amount of wetting agent added may range from 0.01% to 1% by weight of the suspending fluid, but is preferably between 0.01% and 0.1%. In order to prevent foaming of the suspending fluid/polymer particle grinding aid mixture during agitation, a suitable antifoaming agent may be used, typically a silicon or oil-based commercially available antifoam. Generally, no more than 1% of the suspending fluid by weight of

the active antifoaming agent is used. Representative but non-exhaustive examples of antifoaming agents are the trademark of, and sold by, Dow Corning, Midland, Michigan; and Bubble Breaker products, trademark of, and sold by, Witco Chemical Company, Organics Division. Mix tank 150 may be blanketed with a non-oxidizing gas such as nitrogen, argon, neon, carbon dioxide, carbon monoxide, gaseous fluorine, or chlorine, or hydrocarbons such as propane or methane, or other similar gases, or the non-oxidizing gas may be sparged into mix tank 150 during polymer particle addition to reduce the hazard of fire or explosion resulting from the interaction between the small polymer particles.

After the suspending fluid/polymer/particle mixture grinding aid is agitated to form a uniform mixture, a thickening agent may be added to increase the viscosity of the mixture. The increase in viscosity retards separation of the suspension. Typical thickening agents are high molecular weight, water-soluble polymers, including polysaccharides, xanthum gum, carboxymethyl cellulose, hydroxypropyl guar, and hydroxyethyl cellulose. Where water is the suspending fluid, the pH of the suspending fluid should be basic, preferably above 9, to inhibit the growth of microorganisms.

The product resulting from the agitation in the mix tank is a stable suspension of a drag-reducing polymer in a suspending fluid suitable for use as a drag-reducing agent. This suspension may then be pumped or otherwise transported to storage for later use, or used immediately.

The liquid refrigerant, as well as the suspending fluid, grinding aid, partitioning agent, detergent, antifoaming agent, and thickener, should be combined in effective amounts to accomplish the results desired and to avoid hazardous operating conditions.

These amounts will vary depending on individual process conditions and can be determined by one of ordinary skill in the art. Also, where temperatures and pressures are indicated, those given are a guide to the most reasonable and best conditions presently known for those processes, but temperatures and pressures outside of those

5 ranges can be used within the scope of this invention. The range of values expressed as between two values is intended to include the value stated in the range.

CLAIMS

1. A method for the preparation of a drag-reducing polymer suspension comprising:
 - a) mixing an ultra-high molecular weight polymer with an atmosphere comprising refrigerant, and oxygen, air, or mixtures of oxygen and air;
 - b) grinding the polymer at a temperature below the glass transition of the ultra-high molecular weight polymer to form ground polymer; and
 - c) mixing the ground polymer with a suspending fluid to form the drag-reducing polymer suspension.
2. The method as described in claim 1, wherein the ultra-high molecular weight polymer comprises a linear poly(α -olefin) produced from one or more α -olefin monomers with carbon chain lengths of between four and twenty carbons, or mixtures of two or more such linear poly(α -olefins).
3. The method as described in claim 1, wherein: the refrigerant is selected from the group consisting of liquid nitrogen, liquid helium, liquid argon, dry ice, and mixtures thereof.
4. The method as described in claim 1, further comprising prior to step b): mixing the polymer with a grinding aid.
5. The method as described in claim 4, wherein the grinding aid has a melting point of about -100°C to about 25°C .
6. The method as described in claim 4, wherein the amount of grinding aid mixed with the polymer comprises less than 50% by weight of the total mixture.
7. The method as described in claim 1, wherein the amount of percentage oxygen in the atmosphere is greater than 4%, by volume.
8. The method as described in claim 7, wherein the amount of oxygen in the atmosphere is greater than 6%, by volume.
9. The method as described in claim 1, wherein the suspending fluid comprises water or an oxygenated organic solvent.

10. The method of claim 9, wherein the suspending fluid further comprises a suspension stabilizer.
11. The method of claim 9, wherein the suspending fluid further comprises one or more components selected from the group consisting of a detergent, an anti-foaming agent, and a thickening agent.
12. A method for the preparation of a drag reducing suspension comprising:
- (a) cooling an ultra-high molecular weight polymer to less than about 30°C;
 - (b) chopping the polymer to form a chopped polymer;
 - (c) pre-cooling the chopped polymer to a temperature below the glass transition temperature of the polymer in a pre-cooler apparatus;
 - (d) mixing the chopped polymer with a partitioning agent to form a polymer/partitioning agent mixture;
 - (e) injecting oxygen, air, or mixtures thereof into the pre-cooler apparatus;
 - (f) grinding the polymer/partitioning agent mixture at a temperature below the glass transition temperature of the polymer to form ground polymer; and
 - (g) mixing the ground polymer above the glass transition temperature of the polymer with a suspending fluid.
13. The method as described in claim 12, wherein the ultra-high molecular weight polymer comprises a linear poly(α -olefin) produced from one or more α -olefin monomers with carbon chain lengths of between four and twenty carbons, or mixtures of two or more such linear poly(α -olefins).
14. The method as described in claim 12, further comprising prior to step f):
mixing the chopped polymer with a grinding aid.
15. The method as described in claim 14, wherein the grinding aid has a melting point of about -100°C to about 25°C.
16. The method as described in claim 14, wherein the amount of grinding aid mixed with the chopped polymer comprises less than 50% by weight of the total mixture.
17. The method as described in claim 12, wherein the amount of percentage oxygen in the atmosphere is greater than 4%, by volume.

18. The method as described in claim 17, wherein the amount of oxygen in the atmosphere is greater than 6%, by volume.

19. The method as described in claim 12, wherein the suspending fluid comprises water or an oxygenated organic solvent.

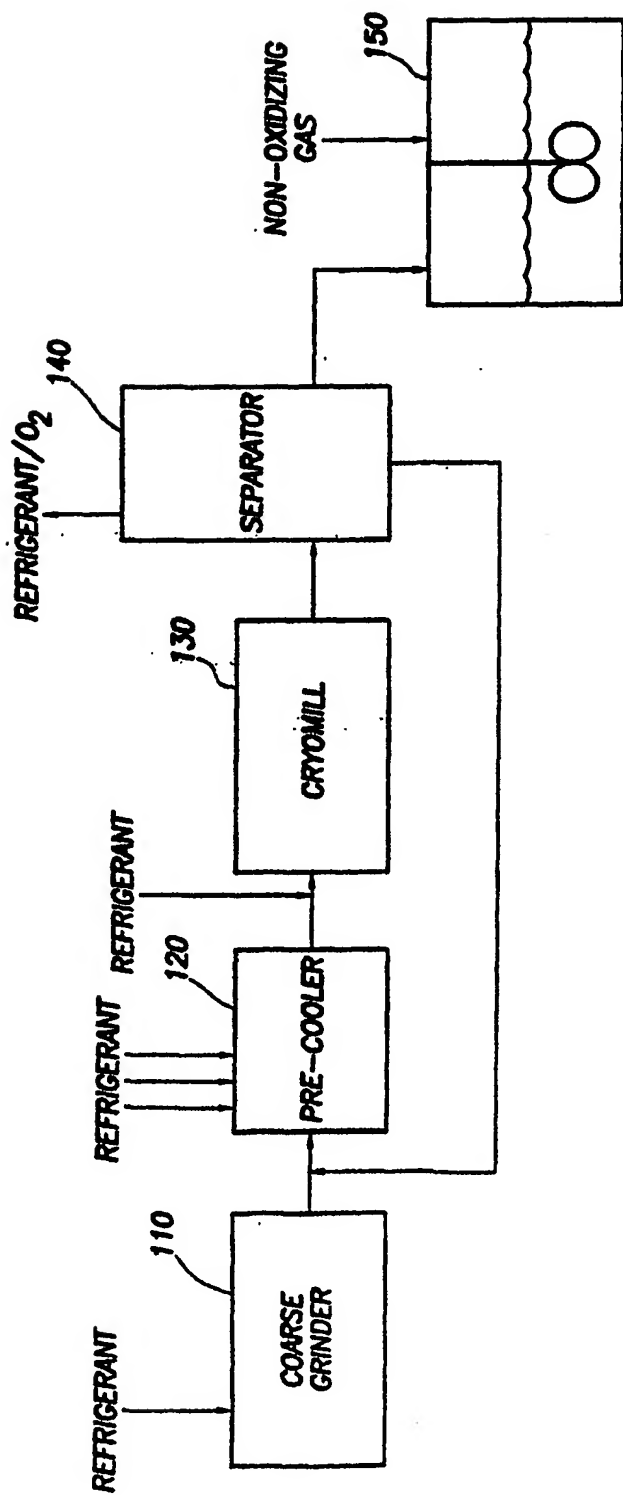


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/30816

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J3/05 C08J3/12 B02C19/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J B02C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 5 539 044 A (MASSOUDA DEBORA F ET AL) 23 July 1996 (1996-07-23) column 8, line 17-49 column 11, line 53 -column 15, line 36; claims; example 5	1-11 12-19
X	WO 97 32926 A (CONOCO INC) 12 September 1997 (1997-09-12) page 8, line 33 -page 13, line 15 page 15, line 16-21 page 24, line 23 -page 29, line 15; claims; example 5	1-11
X	US 5 244 937 A (ADAMS WILL G ET AL) 14 September 1993 (1993-09-14) column 3, line 1 -column 6, line 25; claims; examples	1-11
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z document member of the same patent family

Date of the actual completion of the international search

5 December 2002

Date of mailing of the international search report

16/12/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3018

Authorized officer

Otegui Rebollo, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/30816

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 771 729 A (FRABLE N) 13 November 1973 (1973-11-13) column 1, line 43 -column 5, line 52; claims; figures ---	1-19
A	US 4 273 294 A (HOLLELY DAVID J E ET AL) 16 June 1981 (1981-06-16) column 1, line 5 -column 2, line 50; claims ---	1-19
A	US 4 826 728 A (O'MARA DION P ET AL) 2 May 1989 (1989-05-02) cited in the application column 4, line 18-33; claims -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/30816

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5539044	A	23-07-1996	CA 2247100 A1	12-09-1997
			WO 9732926 A1	12-09-1997
			EP 0885259 A1	23-12-1998
			NO 984113 A	09-11-1998
WO 9732926	A	12-09-1997	CA 2247100 A1	12-09-1997
			US 5539044 A	23-07-1996
			WO 9732926 A1	12-09-1997
			EP 0885259 A1	23-12-1998
US 5244937	A	14-09-1993	NO 984113 A	09-11-1998
			CA 2247100 A1	12-09-1997
			US 5539044 A	23-07-1996
			WO 9732926 A1	12-09-1997
			EP 0885259 A1	23-12-1998
			NO 984113 A	09-11-1998
			AU 649371 A1	19-05-1994
			CA 2098221 A1	12-12-1994
			EP 0626418 A1	30-11-1994
			FI 932123 A	12-11-1994
			NO 931710 A	14-11-1994
US 3771729	A	13-11-1973	AT 170893 T	15-09-1998
			DE 69320943 D1	15-10-1998
			DE 69320943 T2	04-02-1999
			DK 626418 T3	22-02-1999
			ES 2121894 T3	16-12-1998
			CA 985665 A1	16-03-1976
			DE 2223769 A1	21-12-1972
US 4273294	A	16-06-1981	FR 2142523 A5	26-01-1973
			GB 1340312 A	12-12-1973
			IT 957727 B	20-10-1973
			ZA 7201507 A	25-04-1973
			GB 2044126 A	15-10-1980
US 4826728	A	02-05-1989	BR 8001553 A	11-11-1980
			CA 1149357 A1	05-07-1983
			DE 2964039 D1	23-12-1982
			EP 0017368 A1	15-10-1980
			MX 149975 A	21-02-1984
			ZA 8001490 A	25-03-1981
			US 4720397 A	19-01-1988
US 4826728	A	02-05-1989	AT 87511 T	15-04-1993
			AU 595300 B2	29-03-1990
			AU 7021487 A	30-06-1987
			CA 1315160 A1	30-03-1993
			DE 3688200 D1	06-05-1993
			DE 3688200 T2	21-10-1993
			DK 416387 A	12-10-1987
			EP 0289516 A1	09-11-1988
			JP 7068356 B	26-07-1995
			JP 1500357 T	09-02-1989
			NO 873346 A ,B,	12-10-1987
			NO 912565 A ,B,	12-10-1987
			WO 8703516 A1	18-06-1987
			US 4789383 A	06-12-1988
			US 4837249 A	06-06-1989
			US 4758354 A	19-07-1988